

Potato peeling costreams as raw materials for biopolymer film preparation

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ABSTRACT: Potato peel mass is a costream produced in large quantities by the food industry. Its availability and the presence of starch (46%), pectin, and cellulose make it a potential renewable raw material for polymer products. In this study, biopolymer films were produced from potato peel mass and glycerol. High-pressure homogenization (HPH) and HPH combined with heat treatment were investigated as pretreatment technologies before film casting. HPH-treated potato peel mass yielded biopolymer films with similar barrier and mechanical properties as films prepared from pure potato starch, including complete impermeability to grease. Additional heat treatment of the peel mass enhanced starch gelatinization, resulting in improved barrier properties and smoother surface topography of the films. Films with similar appearance and quality were also obtained from starch-free potato peel mass, indicating that potato fiber rich in pectin and cellulose is likewise a suitable material for biopolymer film preparation after HPH treatment. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42862.

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INTRODUCTION

There is growing interest in the use of agricultural and food industry costreams for the development of biodegradable materials. Biopolymers have potential to replace petroleum-based polymers, for example, in packaging applications.¹ Potato is the world's fourth most important food crop, with an estimated annual production of 376 million tons in 2013.² A large proportion of potato, especially in North America and Europe, is consumed in processed form, for example, as frozen products, chips, and French fries.³ In 2013, 64% of all potato produced in the United States was consumed in processed form.⁴ Processing typically involves removal of potato peels by heat, NaOH, or abrasive techniques. Peeling results in a substantial costream that is generally used as animal feed for local farms or treated as waste.⁵ For potato processors, the costreams are of zero or negative value. The wet costreams are prone to microbial spoilage, which makes handling and disposal difficult. In the major European French fry plants, the average weight loss of potatoes due to heat peeling is 9.6%.⁶ In prepeeled potato products, 5–24% weight loss due to peeling have been reported.⁷ In addition to peeling, other processing steps generate additional costreams that exacerbate the waste disposal problem.

Despite their negative market value, costreams that arise from potato peeling are an interesting source of polymeric carbohy-

drates, antioxidants, and glycoalkaloids and have the potential to be processed into more valuable products. For instance, potato peeling costreams have been considered for the extraction of antioxidative phytochemicals, for isolation of cellulose nanocrystals for composite materials, as dietary fiber supplements in extruded food products, and as growth media in fermentation processes.^{8–11} Production of film coatings is one option for turning such costreams into higher-value products. Various studies have addressed the use of starch or specifically potato starch as a renewable component in film preparation.^{12,13} Films prepared from starch and glycerol have been shown to biodegrade rapidly both in an aquatic environment and in compost.¹⁴ Because of the disruption of starch granules during processing, starch films also degraded more rapidly than native granular starch during enzymatic hydrolysis.¹⁵ Only limited attention has been given to starch-rich potato peeling costreams as a raw material for biofilm preparation.¹⁶ Besides starch, the other biopolymers present in potato peel (cellulose, pectin, protein, and suberin) may have beneficial effects on film formation and film properties. Nonstarch polysaccharides are structural components of the cell walls, constituting an interconnected network where cellulose microfibrils are embedded in a gel-like matrix of pectin and hemicellulose.¹⁷ Hydrogen bonding and covalent crosslinking play a role in the interaction of these biopolymers. Unlike in citrus peels where high-ester

homogalacturonan is the major pectic polysaccharide, pectin in potato is mainly composed of rhamnogalacturonan I. Potato pectins are typically highly acetylated and show a low degree of esterification, which influences their gelling properties and application potential in relation to pectins from other species.¹⁸

In this work, film preparation from potato peel mass was studied, and the effect of high-pressure homogenization (HPH) and combined HPH and heat treatment on film formation and film properties was examined. HPH (also called microfluidization) is a technique that is widely applied in the pharmaceutical, chemical, and food industries for particle size reduction and texture tailoring. In HPH, a suspension of solid particles is conducted with high speed into multiple thin channels, after which the pressurized streams are collided to each other to produce high shear and impact forces which disintegrate the particles. Properties of potato peel films were compared with the properties of films prepared from pure, commercially available potato starch and from starch-free potato peel mass enriched in fiber (cellulose and pectin). After HPH and heat treatment, wet potato peel slurry was found to be a suitable material to produce films with barrier properties comparable with pure starch films. The material was found to have good film-forming properties even after removal of starch, probably due to the presence of pectin as another film-forming component.

EXPERIMENTAL

Materials

Fresh potato peel was obtained from Satotaito Oy (Huittinen, Finland) where potatoes of the Nicola variety were carefully washed and peeled mechanically without any chemical treatment. Potatoes were lightly peeled to obtain only the outermost layers of tubers in the peel fraction. After peeling, the peel mass was instantly cooled and stored frozen at -20°C . Right after peeling, the mass developed a brownish color due to oxidative reactions that start when potato tissue structure is broken.¹⁹ Commercial potato starch flour was obtained from Finnmyl Oy (Kokemäki, Finland).

Wet Milling and Preparation of Starch-Free Potato Peel Fraction

Thawed potato peel mass was wet-milled in a grinder (MKCA6-2; Masuko Sangyo, Japan) by passing the material first five times through a 0.25-mm gap and then another five times through a 0.2-mm gap. Rotation speed of the grinding stone (MKGA6-120; Masuko Sangyo) was 1500 rpm. The milled peel mass had a total dry matter content of about 12% (w/v). Part of the wet-milled peel mass was subjected to starch removal using an enzymatic method: the mass was diluted to 5% solid content with ultrapure water. The pH of the suspension was adjusted to 6 using 10M NaOH, and the mass was heated at 90°C to gelatinize starch. The heated peel mass was treated with Thermamyl 120L α -amylase (1 mg enzyme protein/g dry raw material; Novozymes, Denmark) for 2 h at 90°C in the presence of 40 ppm (w/v) CaCl_2 , followed by treatment with AMG 300L glucoamylase (1 mg enzyme protein/g dry raw material; Novozymes) for 17 h at 60°C . The soluble starch hydrolysate was removed by filtration through a 90- μm wired cloth. The solid

starch-free peel fraction was washed three times with ultrapure water to remove all remaining soluble components.

Chemical Composition of Potato Peel Fractions

The chemical composition of wet-milled potato peel mass and starch-free potato peel fraction was determined. Moisture content of the samples was determined based on their weight loss after overnight oven-drying at 105°C . Both samples were freeze-dried prior to compositional analysis. Digestible starch was determined enzymatically using a commercial starch assay kit (Megazyme, Ireland).²⁰ Protein concentration was determined based on the total nitrogen content analyzed by the Kjeldahl method.²¹ The total nitrogen content was converted to protein content by multiplying by a factor of 6.25. Ash content was quantified by weighing the incombustible material after combustion in an N 11 muffle furnace (23 h, 550°C ; Nabertherm GmbH, Germany).

Total lipid content of the peel fraction was quantified by heptane extraction in a Soxhlet apparatus for 5 h. The analysis was based on the dry weight of heptane-extracted material. For analysis of cellulosic carbohydrates and lignin, the samples were hydrolyzed with 70% sulfuric acid for 1 h at 30°C followed by hydrolysis with 4% sulfuric acid for 50 min at 120°C using the Laboratory Analytical Procedure: Determination of Structural Carbohydrates and Lignin in Biomass.²² Glucose released into the acid hydrolysate was analyzed by high-performance anion-exchange chromatography with pulse amperometric detection using an ICS-3000 ion chromatography system equipped with a CarboPac PA1 column (Dionex, CA).²³ In data analysis, glucose originating from starch was subtracted from the total amount of glucose released in the acid hydrolysis. The nonstarch glucose obtained from this calculation originates mainly from cellulose, whereas a minor proportion is likely to originate from xyloglucan. Acid-soluble lignin was measured spectrophotometrically at 215 and 280 nm from the acid hydrolysate.²⁴ Acid-insoluble lignin was determined as the dry weight of the insoluble acid hydrolysis residue. Sugars originating from pectin and hemicellulose were analyzed using acid methanolysis with 3-h methanolysis time followed by the analysis of liberated sugars with gas chromatography.²⁵

High-Pressure Homogenization

Wet-milled potato peel mass, starch-free peel fraction, and commercial potato starch were soaked in ultrapure water at 2% (w/v) total dry matter content and mixed using a spoon for a couple of seconds. The samples were fed into the high-pressure homogenizer with two Z-type chambers (M-110EH-30; Microfluidics). The first pass was through chambers having a diameter of 400 μm and 200 μm , and the next three passes were through the 400- μm and 100- μm chambers. The operating pressure was 1500 bar.

Film Formation

The HPH-treated potato peel mass, HPH-treated starch-free peel fraction, and HPH-treated potato starch were used to prepare films. All the samples were adjusted to 2% (w/v) dry matter content with ultrapure water. Glycerol was added and premixed with a spoon at concentrations 10, 20, and 30% (w/w) of dry weight. The samples were further mixed with a

SpeedMixer (DAC 110.1 VAC-p; Hauschild, Germany) for 5 min at 1600 rpm. The mixing was performed under 100% vacuum to prevent the formation of air bubbles before film casting. The film-forming solutions (40–50 mL) were cast onto polystyrene Petri dishes Ø 13.5 cm and dried for 2 days at ambient conditions. The films were stored at 23°C and 50% relative humidity before testing of barrier and mechanical properties. All tests were performed within 1 month of film casting.

As an alternative approach, the HPH-treated potato peel mass and potato starch suspensions were further heat-treated before film casting to verify if an additional heating step would improve starch gelatinization and thus beneficially affect film formation. The additional heat treatment step (90°C, 10 min) was applied after glycerol addition and prior to final mixing with the SpeedMixer. The starch-free peel fraction had undergone a heating step as part of enzymatic starch removal, and therefore, an additional heating step was not applied for this material.

Appearance and Microstructure of Peels and Prepared Films

Thickness of the dried films was measured using an L&W Micrometer 51 (Lorentzen & Wettre, Sweden). Film thickness was found to vary between 60 and 90 µm. Digital photographs of the films were taken. UV–visible light absorption of the films between 200 and 800 nm was determined using an UV spectrophotometer. Absorbance (A) was converted into transmittance-% ($%T$) by using the following equation: $A = 2 - \log_{10} \%T$. A scanning electron microscope (SEM; JEOL JSM-6360LV) with accelerating voltage control of 10 kV was used to visualize the upper surface topography of the films. For optical microscopy, aqueous suspensions of the samples were spread onto microscopy slides and dried. Starch was stained with 1:10 diluted Lugol's iodine solution (I_2 0.33% w/v, and KI 0.67% w/v), and protein was stained with aqueous 0.1% (w/v) Light Green for 1 min (BDH Chemicals, UK). When imaged in brightfield, iodine-stained starch granules appear dark blue and Light Green-stained protein appears green. Cross-cut surfaces of the films were imaged based on their autofluorescence without staining using excitation at 330–385 nm and detection of emission at >420 nm. The samples were imaged with an Olympus BX-50 microscope (Olympus, Japan). Micrographs were obtained using a PCO SensiCam CCD color camera (PCO AG, Germany) and the Cell[^]P imaging software (Olympus). Images taken from replicate samples were examined, and representative images were selected for publication.

Moisture Resistance

Solubility studies using a water bath were carried out using Ika-Vibrax-VXR (Type VX 2; Janke & Kunkel, Germany). Film strips were immersed in distilled water and kept under constant shaking (200 rpm) for 5 days at 23°C. Water contact angles of the films were measured using CAM200 equipment (KSV Instruments, Finland) in test conditions of 23°C and 50% relative humidity. Water vapor transmission rates of the films were determined gravimetrically using a modified ASTM-E-96A procedure “desiccant method.” Samples with a test area of 30 cm² were mounted on a circular aluminum dish (68-3000 Vapometer EZ-Cups; Thwing-Albert Instrument Company) containing

Table I. Chemical Composition of Potato Peel Mass and the Starch-Free Potato Peel Fraction

Sample Component	Potato peel (% d.m.)	Starch-free potato peel (% d.m.)
Starch	46.2	Nd
Nonstarch polysaccharides	26.6	72.5
Rha	0.9	1.9
Ara	3.0	7.2
Gal	8.2	16.8
GalA	7.1	14.2
Glc	5.8	28.6
GlcA	0.2	0.6
Xyl	1.1	2.6
Man	0.3	0.6
Fru	0	0
Soluble sugars	0.8	0.2
Lignin-like polyphenolics	7.0	10.9
Acid-soluble	2.0	2.8
Acid-insoluble	5.1	8.1
Crude protein	6.4	8.4
Ash	2.8	2.7
Crude fat	Na	0.6
Undetermined	10.2	4.7

Nd, not detected; Na, not analyzed; d.m., dry matter.

dry calcium chloride (0% relative humidity). The dishes were stored in test conditions of 23°C and 50% relative humidity and weighed periodically until a constant rate of weight gain was attained. Climaveneta climate control system (Italy) model AXO 10 was used to control both temperature and humidity conditions in an environmental room. Humidity gradient is the driving force for water molecules to diffuse within a material. In this test, a 50/0% relative humidity gradient was used. Therefore, water molecules were transported from the higher humidity environment into the cups toward the desiccant, calcium chloride. The water contact angle and water vapor transmission measurements were performed in triplicate for each type of film.

Oxygen Transmission

Oxygen transmission rates through the films were determined according to the standard ASTM D-3985 procedure using Oxygen Permeation Analyser Models 8001 and 8011 (Systech Instruments, UK). The analyzer offers fully automated temperature, humidity, and flow control providing consistent and repeatable test conditions. Duplicate measurements for each type of film were performed. The test area of the samples was 50 cm². Because of brittleness, some of the samples were tested with metal masks with a reduced test area of 5 cm². The tests were carried out at 23°C at 0 and 80% relative humidity using 100% oxygen as a test gas.

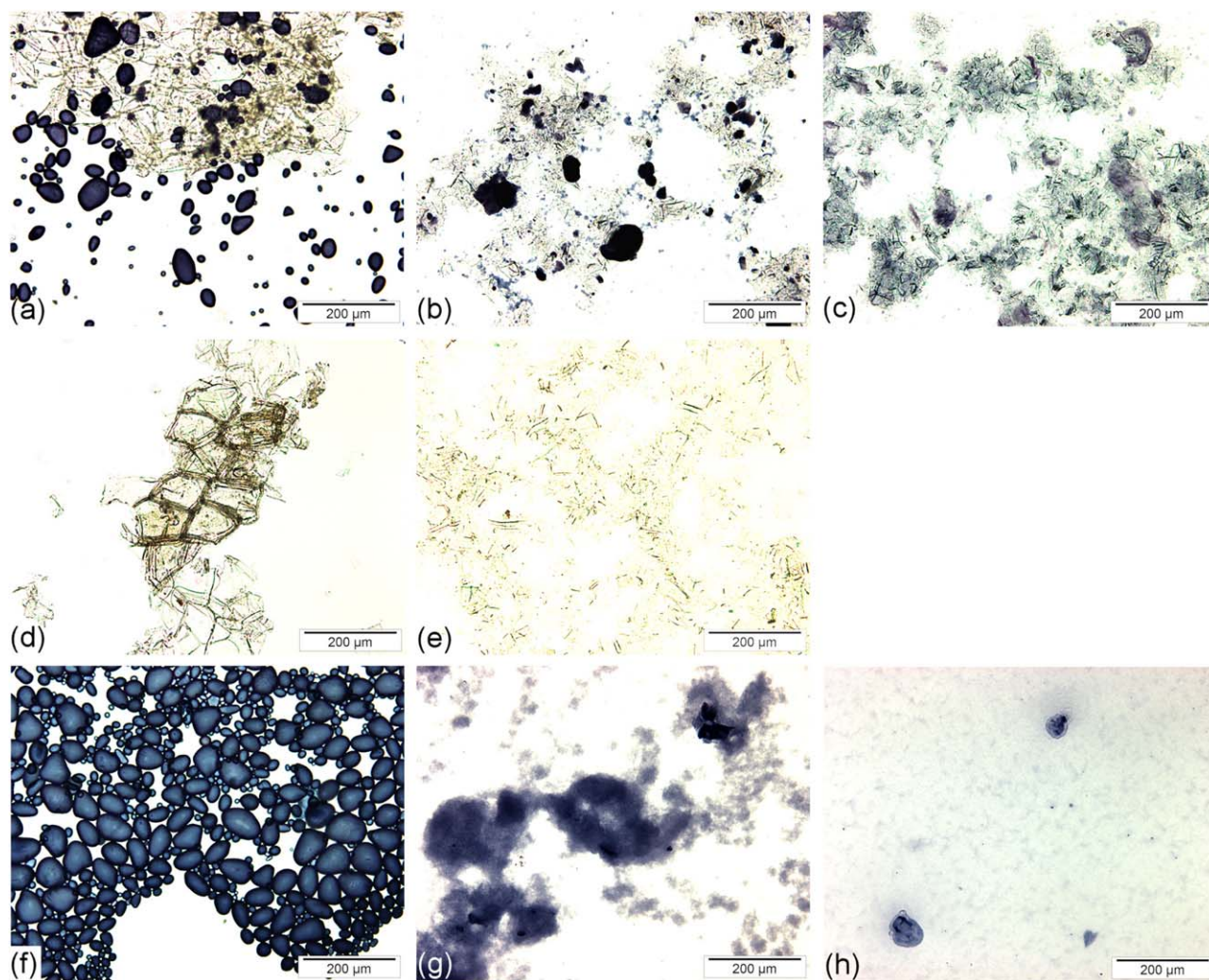


Figure 1. Microstructure of potato peel mass (a–c), starch-free peel fraction (d and e), and potato starch (f–h). Images (a), (d), and (f) represent samples before treatment, (b), (e), and (g) represent samples after high-pressure homogenization (HPH), and (c) and (h) represent samples after combined HPH and heat treatment (HPH + H). All the samples were visualized by brightfield microscopy with prior staining of starch and proteins with Lugol's iodine and Light Green, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Grease Penetration

Grease penetration was determined according to a modified Tappi T 507 method using four replicate samples of each type of film. First, standard olive oil was colored with Sudan II dye and applied onto 5 cm × 5 cm sized blotting paper. A stain-saturated piece of blotting paper was placed against one side of the films, and a piece of blank blotting paper (stain absorber) was placed against the other side. The whole stack was pressed between two plates and kept in an oven at 60°C for 4 h. At the end of the test period, the assembly was removed, and the stain absorbers were examined. For each absorber, the area and the number of stained spots, if any, were determined.

Mechanical Properties

Lloyd 1000R Materials Testing System (Lloyd Instruments, UK) with 100 N load cell was used to determine tensile strength, strain, and Young's modulus of 4–6 replicate samples in test conditions (23°C and 50% RH). Climaveneta climate control system model AXO 10 was used to control both temperature and humidity conditions in an environmental room. The width

of the sample strip was 15 mm, and the gauge distance was 20 mm.

Statistical Analysis

For those film properties which were determined by at least three replicate measurements (water contact angle, water vapor transmission, and mechanical properties), differences between the samples were analyzed using analysis of variance and Tukey's honestly significant difference test (significance of differences at $P < 0.05$) using IBM SPSS Statistics 18 software.

RESULTS AND DISCUSSION

Chemical and Visual Characterization of Raw Materials for Film Preparation

Potato peel mass had a high moisture content of 88%, similar to fresh whole potatoes which typically contain 72–85% moisture.¹⁸ Starch, pectin, cellulose, hemicellulose, lignin-like polyphenolic compounds, and proteins were the major biopolymers present in the peel mass (Table I). Starch (46.2% of dry matter) was clearly the most abundant biopolymer in the peel mass

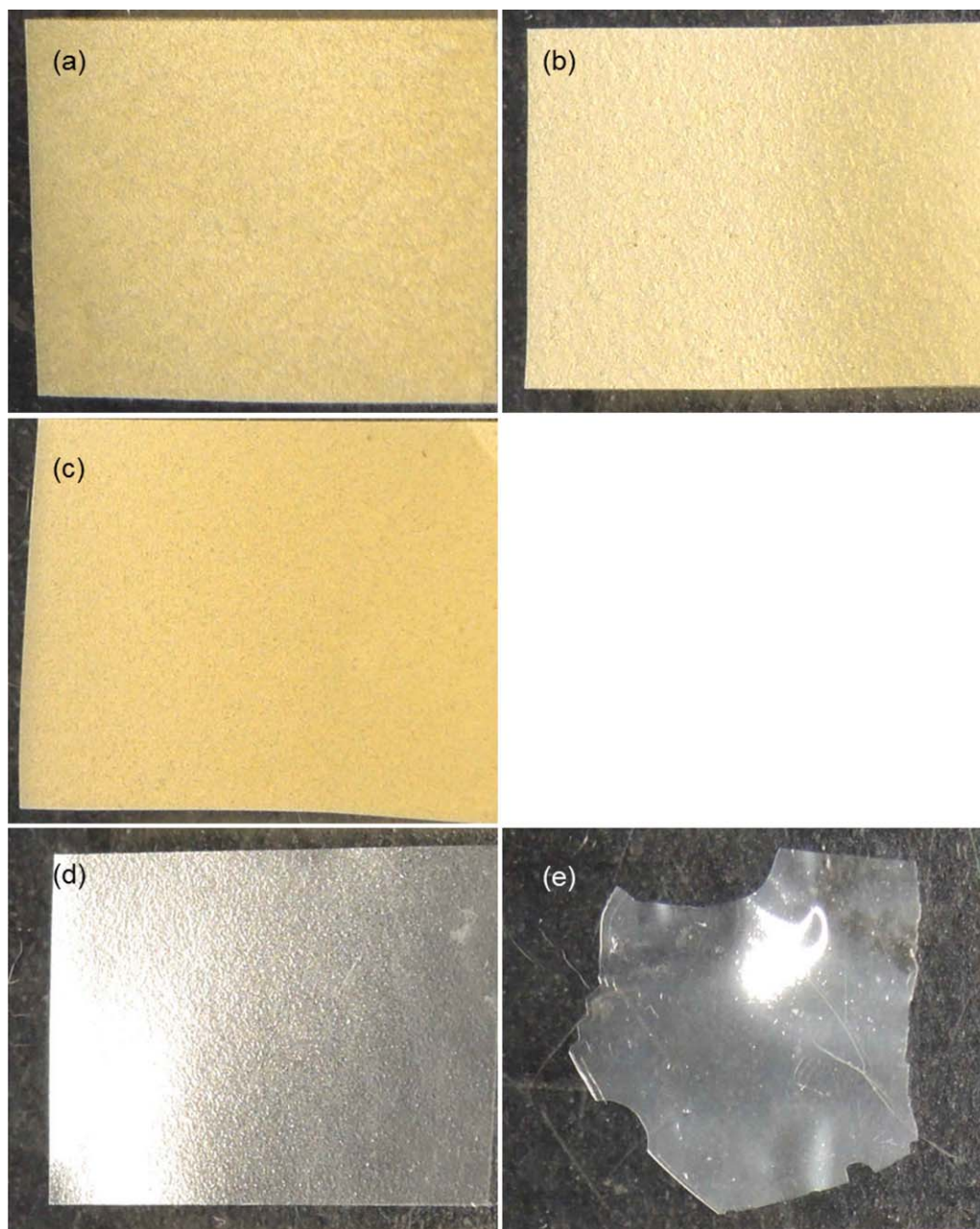


Figure 2. Appearance of films prepared from different potato fractions: potato peel mass (a and b), starch-free potato peel fraction (c), and potato starch (d and e). Films in Panels (a), (c), and (d) were produced from high-pressure homogenized (HPH) samples, and films in Panels (b) and (e) from HPH and heat-treated samples. Approximately 1.5×1 cm pieces of the films were photographed. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(Table I), although the starch content was lower than in fresh potatoes which generally contain 65–85% starch on a dry matter (d.m.) basis.¹⁸ The bulk of a fresh potato is composed of parenchyma cells which are filled with starch granules and surrounded by thin, nonlignified primary cell walls, whereas the potato peel (periderm) cells are characterized by low starch content and thicker, lignified and suberin-containing cell walls.¹⁸ Thus, reduced starch content of the potato peel mass in comparison with fresh potatoes is explained by the higher proportion of periderm cells in the peel mass.

Additionally, a destarched sample was produced by enzymatic removal of starch from the peel mass. According to mass balances, the destarched peel fraction represented 43% of the initial dry weight of potato peel mass. The peel fraction was completely free of starch, indicating complete and selective starch degradation during enzyme treatment. In comparison with the initial peel mass, the starch-free peel fraction had a higher relative content of nonstarch polysaccharides (72.5% of d.m.), lignin-like polyphenolics (10.9% of d.m.), and protein (8.4% of d.m.; Table I). The undetermined proportion of organic dry

matter (4.7% of d.m.) was expected to be suberin-like waxy material, which acts as a protective water barrier in the potato peel.¹⁸ Although starch was naturally the polymer responsible for film formation in potato peel and potato starch films, solubilized pectin was most likely forming the film structure in films made from the starch-free peel fraction.

The starting materials for film preparation were examined before and after HPH/heat treatment by brightfield microscopy. The samples were treated with Lugol's iodine, which stains starch blue but leaves other carbohydrates such as cellulose and pectin unstained (Figure 1 a,d,f). In addition, Light Green dye was used to stain proteins green. Pale green color was detected with higher magnification in the potato cell walls than inside the cells, indicating the association of protein with the cell wall carbohydrates (data not shown). Microscopy images of the starting materials clearly showed that the potato peel mass contained starch granules that were partially free and partially embedded in a fibrous matrix of cellulose- and pectin-rich cell walls (Figure 1a). Starch granules were no longer detected in the starch-free peel fraction (Figure 1d,e) as shown by staining with Lugol's iodine treatment, indicating that destarching of potato peel had completely removed the starch granules. By contrast, the fibrous matrix of cellulose and pectin also appeared to remain intact in the starch-free peel fraction (Figure 1d). The observed tissue fragments were about 500–1000 μm in size. Pure potato starch consisted exclusively of oval-shaped starch granules of approximately 10–50 μm in size (Figure 1f). The size of the granules is in accordance with the literature where sizes of potato starch granules are reported to range from 10 to 100 μm .²⁶

High-pressure homogenization effectively reduced the particle size of the cellulose–pectin matrix to roughly 50–200 μm , both in the potato peel mass (Figure 1b) and in the starch-free peel fraction (Figure 1e). In addition to changes that were visible with light microscopy, HPH treatment has been reported to have pronounced effects on cellulose and pectin at nanometer scale that are likely prerequisites for their film-forming properties: HPH is a well-established method for fibrillation of cellulose to increase its surface area for preparation of strong nanofibrillated cellulose films.²⁷ HPH is also known to degrade and solubilize pectic oligosaccharides from pectin.²⁸ After HPH, potato starch granules had collapsed and the starch appeared as an amorphous mass in the microscopic images due to its partial solubilization (Figure 1g). HPH of cassava starch at 1500 bar has been shown previously to gelatinize 75% of starch granules.²⁹ Another study similarly demonstrates that after 10 passes of HPH at 1380 bar, potato starch granules were no longer visible by light microscopy because of their gelatinization/solubilization.¹⁶ Starch gelatinization during HPH treatment is expected to result from the combined effect of shear forces and increased temperature. In the HPH-treated peel mass, starch granules appeared less uncoiled than in the HPH-treated pure starch sample, suggesting that the cellulose- and pectin-rich matrix protected the starch granules during HPH treatment of the peel mass (Figure 1b). When an additional heat treatment was applied to the HPH-treated potato peel mass, starch appeared completely gelatinized (Figure 1c). By contrast after

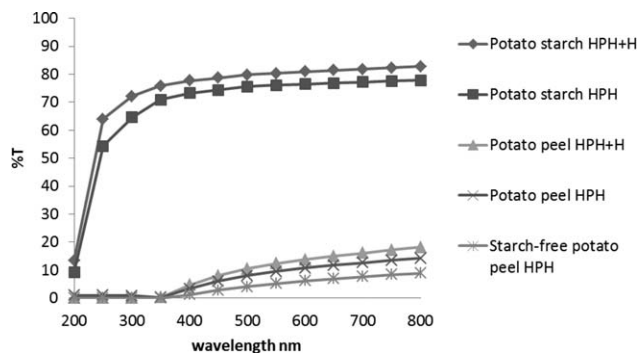


Figure 3. Light transmittance (%*T*) of films prepared from different potato fractions: potato peel mass (a and b), starch-free potato peel fraction (c), and potato starch (d and e). The materials were treated with high-pressure homogenization (HPH) or combined HPH and heat treatment (HPH + H) before film casting.

additional heating of the HPH-treated potato starch sample, the starch was less readily stained with iodine, and the particles were barely visible under the light microscope, suggesting that the molecular weight of starch was substantially reduced or its structure was otherwise changed by additional heat treatment (Figure 1h).

Visual Appearance and Microstructure of Films

Although all films prepared from pure potato starch were clear (Figure 2d,e) and almost completely transparent (%*T* > 80; Figure 3), films prepared from potato peel mass and starch-free peel fraction were brownish and translucent to some extent (Figure 2a–c). The brown color originates from the oxidation reactions that took place instantly after potato peeling¹⁹ and could be prevented by applying chemicals such as NaHSO₃ to the peel mass. Additional heat treatment increased the transparency of both potato peel and potato starch films as determined by measurement of light transmittance (Figure 3).

When examined with the naked eye, all films appeared smooth and homogeneous (Figure 2). Films prepared from HPH-treated potato peel mass without additional heat treatment had a slightly rougher surface and some imperfection in visual appearance (Figure 2a); however, these visual defects were reduced when the HPH-treated potato peel mass was additionally heated before film casting (Figure 2b). SEM images of the surface topography showed that although potato starch films had a perfectly smooth and homogenous upper surface (Figure 4d,e), films made from potato peel mass and starch-free peel fraction had considerably higher surface roughness (Figure 4a,c). In accordance with the observations made with the naked eye, an additional heating step after HPH decreased the roughness of potato peel films to some extent (Figure 4b). The observations indicate that for crude potato peels, HPH was not sufficient to generate smooth films. The incomplete starch solubilization/gelatinization in the HPH-treated peel mass, as revealed by light microscopy (Figure 1b), may explain the slightly heterogeneous appearance of these films. An opposite effect was observed with the starch films: films prepared from HPH-treated potato starch were homogeneous and strong enough to handle; however, films prepared from HPH- and heat-treated potato starch with 10 or

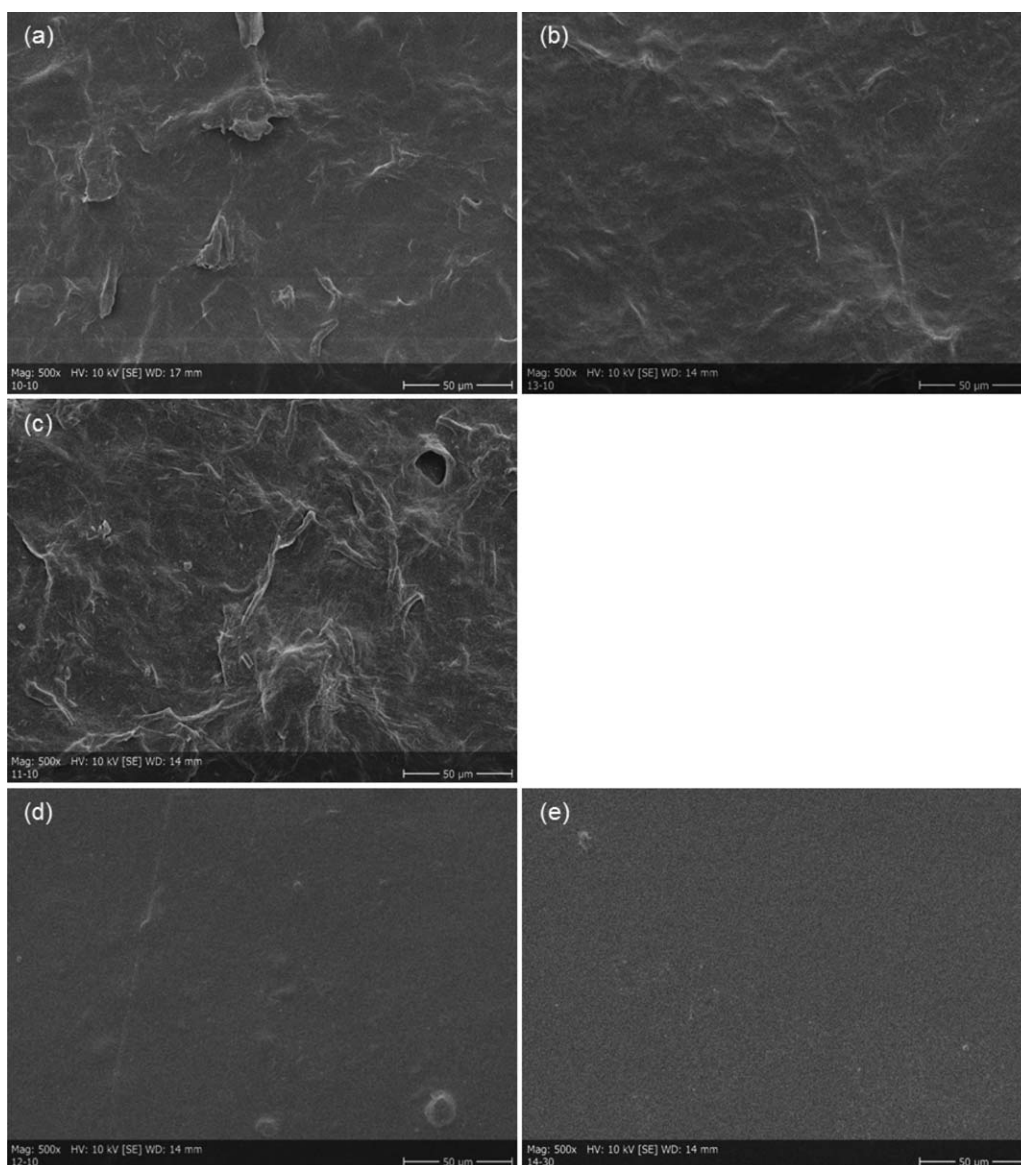


Figure 4. SEM image of the surface topography of films prepared from different potato fractions: potato peel mass (a and b), starch-free potato peel fraction (c), and potato starch (d and e). Films in Panels (a), (c), and (d) were produced from high-pressure homogenized (HPH) samples, and films in Panels (b) and (e) from HPH and heat-treated samples.

20% glycerol were completely shattered on drying and too brittle for any barrier or mechanical property testing.

Light microscopy images taken from cross sections of the films showed respective differences in film morphologies. Films prepared from potato peel mass or starch-free peel fraction had a granular morphology (Figure 5a–c), whereas films from pure starch appeared smoother (Figure 5d,e). The granular appearance of the potato peel films is likely due to the presence of micrometer-scale cellulose- and pectin-rich cell wall particles in the HPH-treated peel mass and HPH-treated starch-free peel fraction (Figure 1b,c,e). The substantial effects of pretreatment were likewise visible in the cross sections: films prepared from HPH- and heat-treated potato peel mass were more densely packed (Figure 5b) than those prepared without additional heat treatment (Figure 5a). The HPH-treated potato starch films had

a layered structure: upper parts of the films appeared rough, whereas lower parts were completely homogeneous (Figure 5d). However, when the potato starch was additionally heated before film casting, the films appeared completely smooth and homogeneous (Figure 5e). The smooth appearance most probably results from the reduced molecular weight of starch due to heat treatment.³⁰ Reduction of molecular weight may also explain the brittle nature of these films.

Barrier and Mechanical Properties of Films

All films were completely impermeable to grease (olive oil) under the test conditions (Table II). Impermeability to grease is a typical and well-known feature of all biopolymer films: in carbohydrate-based films, high surface hydrophilicity and a great number of polar hydrogen bonds enable excellent barrier properties against nonpolar permeants. Grease impermeability

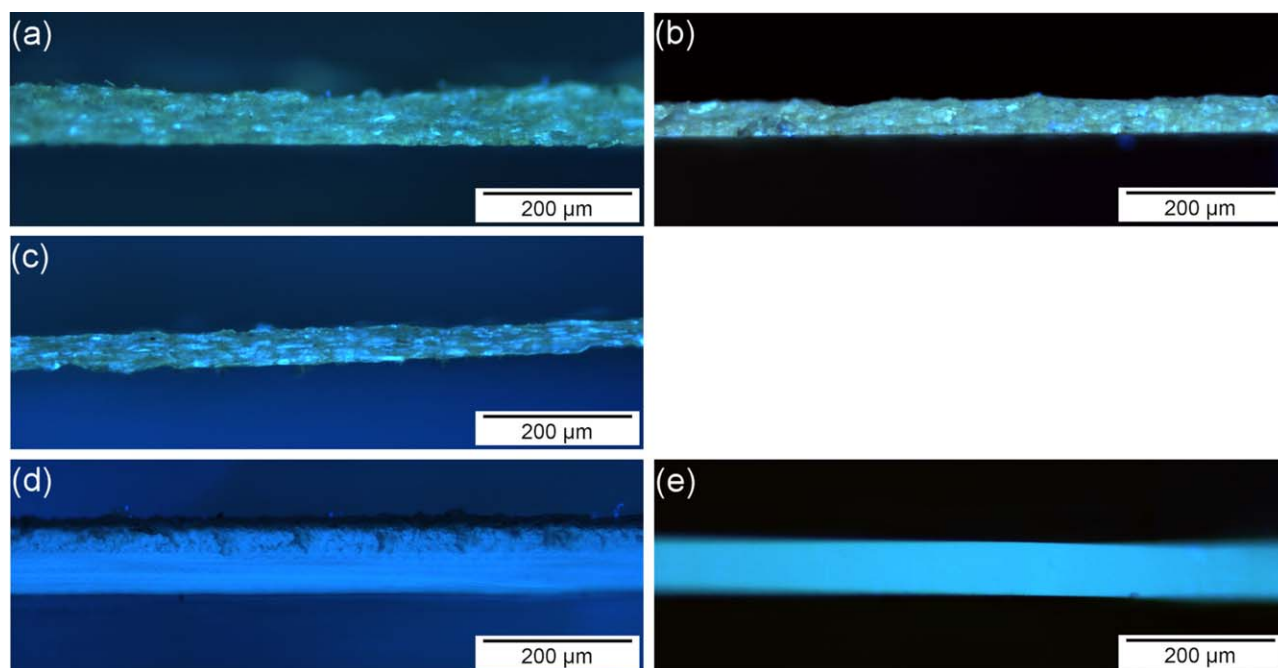


Figure 5. Cross sections of films prepared from different potato fractions: potato peel mass (a and b), starch-free potato peel fraction (c), and potato starch (d and e). Films in Panels (a), (c), and (d) were produced from high-pressure homogenized (HPH) samples, and films in Panels (b) and (e) from HPH and heat-treated samples. All films were visualized using fluorescent microscopy and sample autofluorescence (epifluorescence, excitation 330–385 nm, emission > 420 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

also indicates the absence of cuts and holes in the films. Biopolymer films with excellent grease barrier properties have application potential in food packaging. For example, cardboard containers could be coated with a potato peel film to prevent grease migration from dry and fatty foods such as French fries. At the same time, coatings made from HPH-treated potato peel mass could act as effective mineral oil barriers in recycled cardboard packaging. Recycled cardboard is commonly made out of newspapers and magazines, and may thus contain mineral oil hydrocarbons derived from the printing inks. Recently, migration of mineral oil residues into foodstuffs has been linked to inflammation of internal organs and even cancer,³¹ and therefore, new approaches are needed to prevent mineral oil migration from the packaging materials.

Very low oxygen permeabilities $<10^{-15} \text{ cm}^3 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$ were measured at 0% relative humidity for almost every film (Table II). This result is consistent with the fact that most biopolymers are excellent barrier materials against oxygen transmission in dry conditions because of strong polar interactions between the molecules. However, gas barrier properties of films depend on the molecular mobility of the film-forming matrix, which in turn is very sensitive to moisture variations: water vapor sorption breaks some of the hydrogen bonds that hold the polymer chains together. At high humidity, the films tend to swell, thereby allowing oxygen permeation to increase. Like other biopolymer films, the potato peel and starch films showed clearly increased oxygen permeability at high humidity (80% RH) ($>10^{-13} \text{ cm}^3 \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$; Table II). Water sorption and swelling of films are typically more pronounced at higher glycerol concentrations: glycerol binds to water because of its hygro-

sopic nature, and by reducing hydrogen bonding prevents polymer chains from close packing. In the data presented, oxygen permeability of the films accordingly increased at higher glycerol concentration (Table II).

Films prepared from HPH-treated potato starch were better oxygen barriers at 80% RH than the films from HPH-treated starch-free peel fraction, suggesting that pure starch forms a more effective oxygen barrier than the nonstarch components present in the peel mass. Combined HPH and heat treatment of potato peel mass produced films with improved oxygen barrier properties when compared with HPH treatment only. Overall, the oxygen permeability values were clearly lower when compared with polyethylene and other plasticized starch films, but not as low as in ethylene vinyl alcohol films.¹²

None of the films dissolved in distilled water after constant shaking for 5 days. However, mechanical stability of the films was limited in these conditions, and the films were mostly disintegrated during the test period. The measurement of water contact angle showed that starch content influenced the surface hydrophilicity of the films: potato peel films had lower hydrophilicity than potato starch films ($P < 0.05$, Tukey's test; Table II). The potato peel films showed somewhat higher hydrophilicity than starch-free potato peel films, although without reaching statistical significance. Additional heat treatment slightly increased the hydrophilicity of potato peel films ($P < 0.05$; Table II).

Water vapor permeability results for the films are shown in Table II. Hydrophilic biopolymer films without any hydrophobic modification are typically very poor water barriers, and glycerol

Table II. Hydrophilicity and Barrier Properties of Films Prepared from Potato Peel Mass, Starch-Free Peel Fraction, and Potato Starch after High-Pressure Homogenization (HPH) or after Combined HPH and Heat Treatment

	Glycerol % (w/w d.m.)		Water contact angle (°)		Water vapor permeability ^a ($\text{g}^{-1} \text{s}^{-1} \text{Pa}^{-1}$)		Oxygen permeability, 0% RH ^b ($\text{cm}^3 \text{m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$)		Oxygen permeability, 80% RH ^b ($\text{cm}^3 \text{m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$)		Grease penetration ^c				
	HPH	HPH + H	HPH	HPH + H	HPH	HPH + H	HPH	HPH + H	HPH	HPH + H	HPH	HPH + H			
Potato peel	10	79	EF	58	BCD	4×10^{-11}	ABC	3×10^{-11}	A	9×10^{-16}	8×10^{-16}	1×10^{-12}	4×10^{-13}	0	0
	20	81	EFG	60	CD	7×10^{-11}	F	3×10^{-11}	AB	1×10^{-15}	7×10^{-16}	2×10^{-12}	1×10^{-12}	0	0
	30	80	EFG	53	ABCD	1×10^{-10}	H	4×10^{-11}	ABC	1×10^{-15}	8×10^{-15}	4×10^{-12}	2×10^{-12}	0	0
Starch-free potato peel	10	96	G	NA		4×10^{-11}	BCD	NA		6×10^{-16}	NA	1×10^{-12}	NA	0	NA
	20	86	FG	NA		5×10^{-11}	CDE	NA		2×10^{-15}	NA	2×10^{-12}	NA	0	NA
	30	84	EFG	NA		9×10^{-11}	G	NA		3×10^{-15}	NA	3×10^{-12}	NA	0	NA
Potato starch	10	69	DE	BF		6×10^{-11}	EF	BF		7×10^{-16}	BF	3×10^{-13}	BF	0	BF
	20	41	A	BF		6×10^{-11}	DEF	BF		7×10^{-16}	BF ^d	9×10^{-13}	BF	0	BF
	30	51	ABC	43	AB	9×10^{-11}	G	7×10^{-11}	F	8×10^{-16}	BF ^e	3×10^{-12}	1×10^{-12}	0	0

Glycerol was used as a plasticizer in film preparation. The mean of replicate measurements is reported. Values indicated with different capital letters within one measured parameter differ significantly ($P < 0.05$). Statistical analysis carried out only for water contact angle and water vapor permeability values for which sufficient number of replicate (3) measurements exist. HPH, high-pressure homogenized; HPH + H, high-pressure homogenized and heat-treated; NA, not available; RH, relative humidity.

^a Measurement conditions: 50/0% RH, 23°C, dry cup.

^b 23°C.

^c 60°C, 4 h.

^d BF, film was too brittle to be tested.

^e BF*, film broke during testing.

Table III. Mechanical Properties of Films Prepared from Potato Peel Mass, Starch-Free Potato Fraction, and Potato Starch after High-Pressure Homogenization (HPH) or after Combined HPH and Heat Treatment

	Glycerol % (w/w d.m.)	Tensile strength (MPa)		Tensile strain at break (%)		Young's modulus (GPa)	
		HPH	HPH + H	HPH	HPH + H	HPH	HPH + H
Potato peel	10	29 ± 5 ^D	38 ± 3 ^{EF}	2 ± 0 ^A	3 ± 0 ^A	1.9 ± 0.1 ^F	1.8 ± 0.1 ^F
	20	25 ± 1 ^{CD}	25 ± 2 ^{CD}	4 ± 0 ^A	6 ± 1 ^{AB}	1.2 ± 0.0 ^{DE}	1.1 ± 0.1 ^D
	30	14 ± 2 ^{AB}	13 ± 1 ^{AB}	11 ± 2 ^{BC}	10 ± 1 ^{BC}	0.5 ± 0.2 ^{AB}	0.6 ± 0.1 ^B
Starch-free potato peel	10	58 ± 7 ^G	NA	3 ± 1 ^A	NA	2.7 ± 0.2 ^G	NA
	20	56 ± 4 ^G	NA	10 ± 1 ^{BC}	NA	2.0 ± 0.1 ^F	NA
	30	40 ± 4 ^F	NA	13 ± 1 ^C	NA	1.3 ± 0.1 ^{DE}	NA
Potato starch	10	42 ± 4 ^F	BF	6 ± 1 ^{AB}	BF	1.8 ± 0.1 ^F	BF
	20	32 ± 3 ^{DE}	BF	4 ± 0 ^A	BF	1.4 ± 0.1 ^E	BF
	30	6 ± 0 ^A	17 ± 6 ^{BC}	52 ± 10 ^D	6 ± 1 ^{AB}	0.3 ± 0.0 ^A	0.9 ± 0.3 ^C

Glycerol was used as a plasticizer in film preparation. The mean and standard deviation of replicate measurements are reported. Values indicated with different capital letters within one measured parameter (tensile strength, tensile strain at break, and Young's modulus) differ significantly ($P < 0.05$). HPH, high-pressure homogenized; HPH + H, high-pressure homogenized and heat-treated; NA, not available; BF, film was too brittle to be tested.

further increases their hygroscopic nature. The penetrating water molecules break a substantial number of intramolecular hydrogen bonds, enabling pronounced plasticization and swelling of the polymer matrix and finally resulting in increased moisture transmission. In the current study, the potato starch films had better oxygen barrier properties but somewhat worse water vapor barrier properties than the potato peel films. All water vapor permeability values ranged between 3×10^{-11} and $1 \times 10^{-10} \text{ g m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$. The values are comparable with those of other plasticized starch and cellophane films but not as low as in polyethylene films.³² Water vapor permeation was generally increased at higher glycerol content, whereas heat treatment before film casting reduced the water vapor permeation ($P < 0.05$ at 20 and 30% glycerol concentration). As a result, films obtained from HPH- and heat-treated potato peel mass showed the best water barrier properties. Interestingly, in the films obtained from HPH- and heat-treated peel mass, glycerol concentration had no clear influence on the water vapor permeability.

Tensile strength and Young's modulus decreased, and strain increased as a function of glycerol concentration in almost all films (Table III). As was explained earlier, glycerol reduces the hydrogen bonding, which can negatively influence the mechanical strength of films. When blended with glycerol, the polymer chains have more freedom to slide against each other, enabling increased flexibility and strain. Without plasticizers, most biopolymer films are too brittle to handle, and thus at least a low amount of glycerol is needed for maintaining their further processability. In the current study, the best mechanical properties were obtained with the starch-free potato peel films (Table III), most probably due to their high cellulose content. In these films, potato pectin is probably responsible for the film-forming capability, whereas cellulose likely provides additional mechanical strength to the films.^{9,33} Potato peel fractions also contained protein (Table I), which may have played a role in film formation.

From an economical point of view, it may not be feasible to remove starch from the potato peeling costream. A starch removal step introduces an additional processing cost without remarkably improving the film forming properties of potato peel mass. On the other hand, the potato starch industry produces potato pulp which is an abundant costream with highly similar composition to the starch-free potato peel fraction and with only few applications at present. As shown in this study, the presence of starch in the peel mass is not a prerequisite for suitable film properties, indicating that potato pulp could also be applicable for biopolymer film preparation.

CONCLUSIONS

Potato peeling costreams may be used without fractionation to prepare biopolymer films with barrier properties comparable with pure starch films. HPH treatment alone induced effective gelatinization and enabled the formation of smooth films from pure potato starch, whereas HPH combined with a heating step was the optimal treatment to produce homogeneous films from wet-milled potato peels. The potato peels retained the film-forming ability even after enzymatic starch removal. In the starch-free potato peel fraction, soluble pectin was likely responsible for film formation, whereas cellulose reinforced the film structure, resulting in films with surprisingly better mechanical properties when compared with the other films. This study demonstrates a simple process that enables the production of a higher-value product from an abundant no-value industrial costream.

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